



## POLITECNICO DI MILANO

DIPARTIMENTO DI CHIMICA, MATERIALI ED INGEGNERIA CHIMICA "Giulio NATTA"

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### Anion-Driven Self-Assembly Processes Based on Halogen-Bonding

Grant No. 063042

Final Report

#### **XB Self-complementary modules:**

In 2004 we reported the successful use of tetrakis(4-iodotetrafluorophenyl)methane **2** as template for inducing the topochemical alignment of olefins (**1**), which could thus undergo a solid state photodimerization reaction in quantitative chemical and stereochemical yields (**3**). Our template operated at two-levels: intramolecular  $\pi\cdots\pi$  interactions pre-organize the template arms, and the alignment of template arms is translated into the alignment of olefins at the distance needed for photoreaction, thanks to the highly directional  $N\cdots I$  halogen bonding (Figure 1).

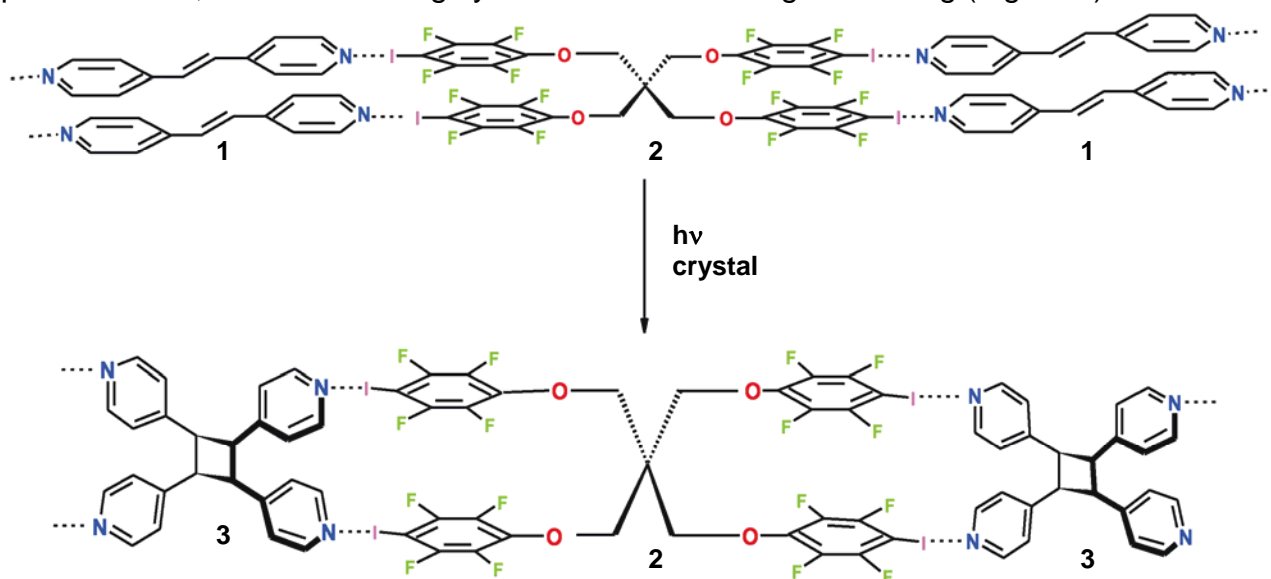


Figure 1

With this in mind, in the first three months of activity of this cooperative agreement, we have synthesized the 1D heteroditopic self-complementary tecton **4** tailored to XB-based self-assembly (Scheme 1). It was designed in order to possess terminal XB-donor and acceptor groups, and to incorporate electron-rich and electron-poor aromatics connected by a double bond. It was expected that such a molecule self-organizes into 1D infinite polar chains thanks to self-complementary XB. Moreover, as a result of heteropolar  $\pi\cdots\pi$  stacking between adjacent chains, the double bonds of the different modules **4** should

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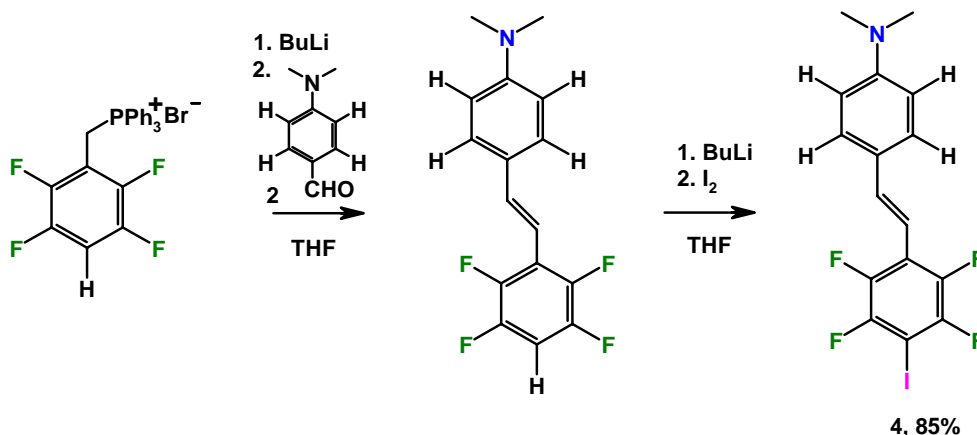
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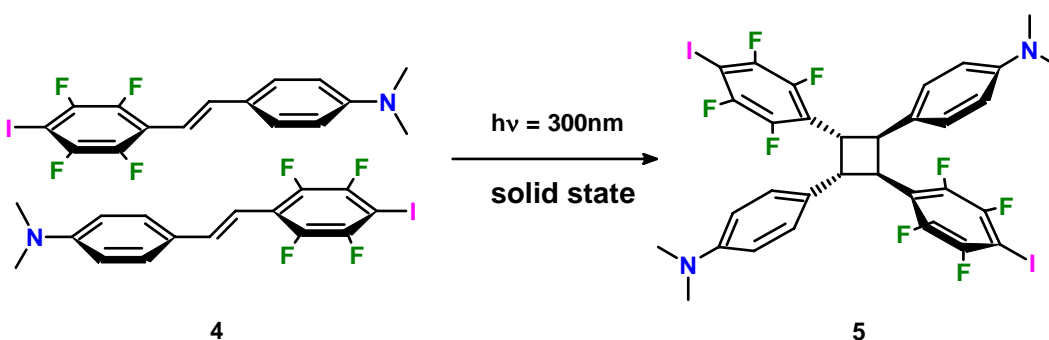
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organize in order to meet the Schmidt's requirements for regiocontrolled photocyclization in the solid state.



**Scheme 1** Synthesis of the 1D heteroditopic self-complementary tecton **4** tailored to XB.

As concerns the supramolecular organization of **4** in the crystal packing, the molecules are arranged in a head-to-tail fashion into 1D infinite chains, as expected for a telechelic self-complementary XB heteroditopic tecton (Figure 2). The head-to-tail arrangement of the dipolar modules **4** ensures that each 1D chain is polar. Coupling of antiparallel 1D dipoles and  $\pi \cdots \pi$  attraction between opposite quadrupolar moments generate a centrosymmetric 2D structure with adjacent chains running in opposite directions. Interestingly, the distance of the centroids of the double bonds for this couple of molecules is only 3.758 Å, nearly a pre-reactive state of the [2+2] reaction. Schmidt's rule is thus respected and the molecule undergoes solid-state cycloaddition by UV photoirradiation (Scheme 2).



**Scheme 2.** Solid state photoreaction of **4** to yield the 2D heterotetratopic self-complementary tecton **5** tailored to XB-based self-assembly.

The photoirradiation at 300 nm for 24 h at room temperature gives the cycloadduct **5** in 80% yield with complete regio- and stereospecificity. The supramolecular organization of **5** in its crystal packing is governed by XB; the cycloadduct **5** possesses two XB donor sites

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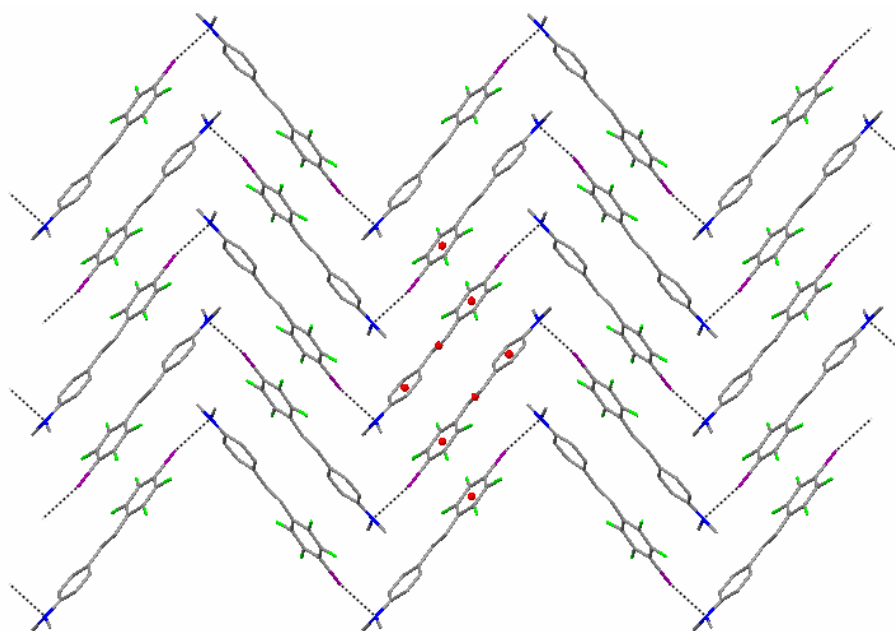
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and two XB acceptor sites and behaves as a 2D heterotetratopic self-complementary tecton. In order to match its multivalency, a 2D infinite network is formed, which has a 4.4 topology, if the molecular centroids are used as nodes (Figure 3). The strength and directionality of the N...I XB prevent the tendency of tecton **5** to pack more efficiently by optimizing its pattern of self-complementary  $\pi\cdots\pi$  stacking interactions. **5** Could form up to eight  $\pi\cdots\pi$  interactions, which are expected to be particularly strong due to the opposite sign of the quadrupolar moments of the involved rings. On the contrary, no such interactions are formed and large columnar voids are present, which are filled in with disordered chloroform molecules. Removal of the clathrated chloroform can be obtained by evaporation at reduced pressure, with the crystals that retain their shapes but become opaque. We have calculated the free space in this crystal by the PLATON software. This resulted in a total potential solvent area volume accessible of 567.3 Å<sup>3</sup> per unit cell, corresponding to the 29.1% of the unit cell volume of the crystal. This value is among the highest reported in the literature for nanoporous organic crystal structures.

Figure 2



This work resulted in a joint publication on the *New Journal of Chemistry* in the special issue dedicated to Supramolecular Chemistry (G. Marras, P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, A. Vij *New J. Chem.* **2006**, 30, 1397) (impact factor (2005) 2.574). For the importance of these results this article has been selected for the design of the front cover of the October issue of the *New Journal of Chemistry*, and it has been also included in the fifth update of *CrystEngSelects*, a selection of articles of interest to crystal engineers from across the RSC journals.

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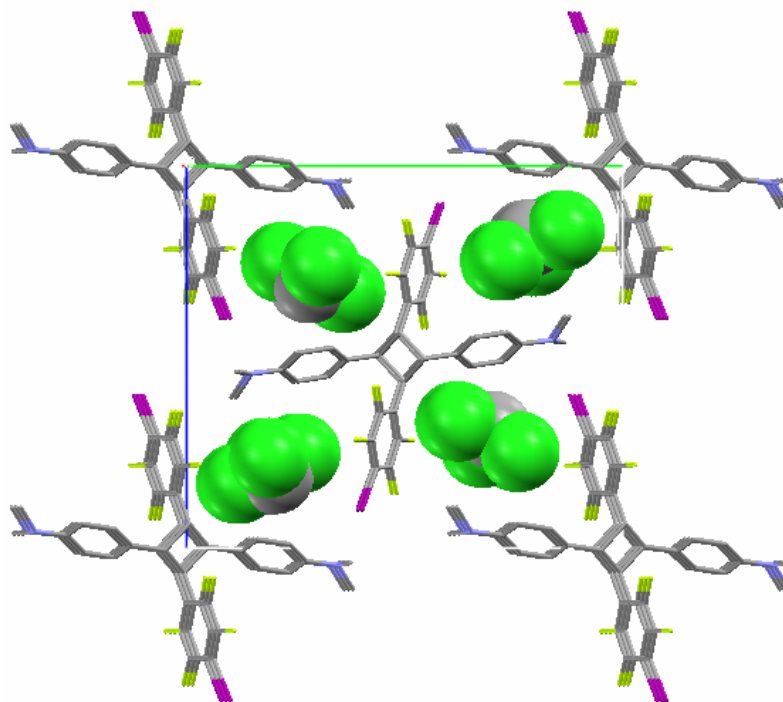
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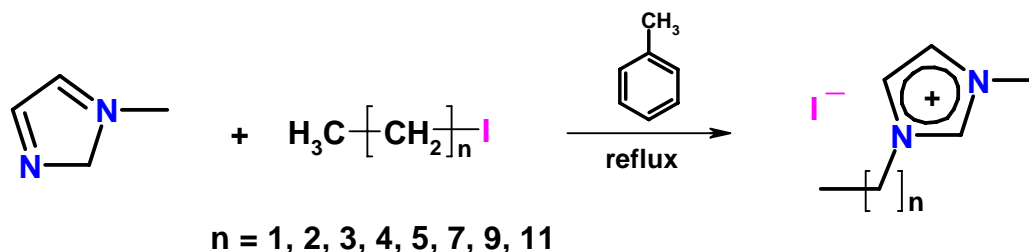
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**Figure 3** A view down the crystallographic *c* axis of the crystal packing of the XB-based self-complementary tecton **5** (ball-and-stick style).

### **XB acceptors:**

During the progress of this research project, a combinatorial approach towards the study of XB-based recognition processes between halo-perfluoroalkanes and naked anions of organic salts as acceptors of electrons has been investigated. Our attention was focused of the iodide salts of different methyl-alkyl-imidazolium cations, for the importance of these materials in the field of ionic liquids (Scheme 3).



**Scheme 3**

As demonstrated from the single crystal X-ray structure of the complex between methyl-ethyl-imidazolium iodide and 1,4-diiodotetrafluorobenzene (Figure 4), the iodide ions are

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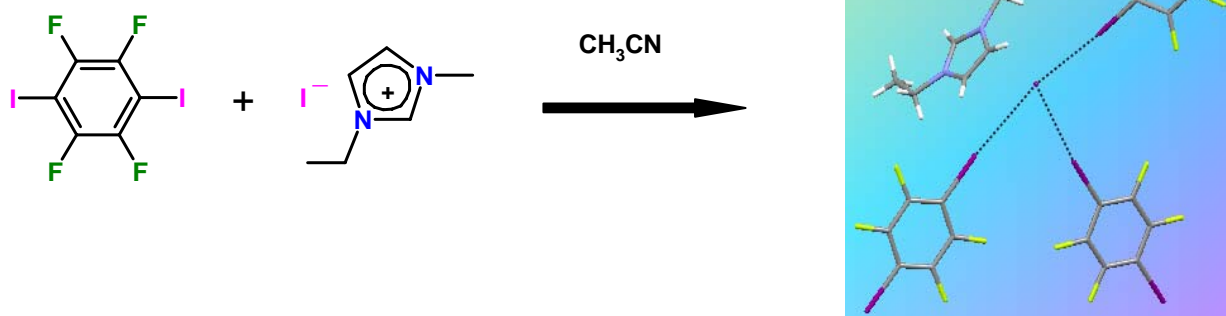
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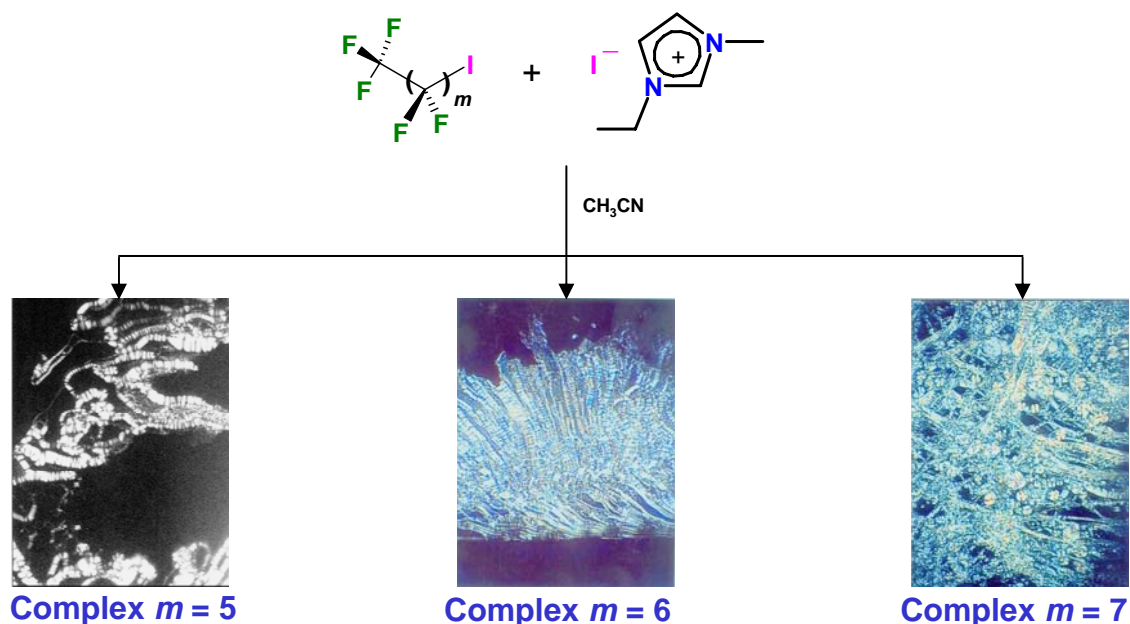
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**Figure 4**

naked enough to coordinate strongly the diiodoperfluorocarbon giving rise to an infinite supramolecular structure. In particular, in the solid state, the iodide anion of 1-methyl-3-ethylimidazolium salt behaves as a tritopic donor towards 1,4-diiodotetrafluorobenzene.

The mesophase behaviour of the complexes between 1-methyl-3-ethylimidazolium iodide and various monoiodoperfluoroalkanes of different length was studied during my visit to the Department of Chemistry of the University of York in December 2005 in collaboration with Prof. Duncan W. Bruce.



**Figure 5**

The fact that these complexes show liquid crystal behavior while made of starting compounds that are not mesomorphic is particularly interesting and open new perspectives in the design of fluorinated ionic liquid crystals.

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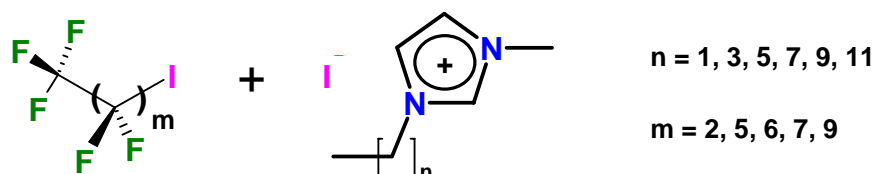
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Keen to extend this approach and to demonstrate its generality we synthesized other methyl-alkyl-imidazolium iodides containing longer alkyl chains (Scheme 4).



**Scheme 4**

The mesophase properties of this kind of ionic supramolecular complexes has been studied in detail, and particular attention has been paid to the reciprocal influence of the length of the alkyl and perfluoroalkyl chains on the type of liquid crystallinity shown by the complexes. This part of work has been conducted in strict collaboration with Prof. Duncan W. Bruce of the Department of Chemistry at the University of York.

Interestingly, despite the nonmesomorphic behaviour of the starting materials all the studied complexes showed liquid crystal properties (smectic phases) as a consequence, probably, of the self-assembly induced by halogen bonding and the stiffness of perfluoroalkyl chains. In fact, all the complexes made of perfluorocarbon chain equal to or longer than 6 carbon atoms, show smectic A phases as it is common for long-chain perfluorocarbons.

As concerns the imidazolium salts, for  $n = 1, 3, 5, 7, 9$  they are not mesomorphic whereas the corresponding halogen-bonded complexes are liquid crystalline. Conversely, with  $n = 11$  the starting imidazolium salt is mesogenic while the corresponding halogen-bonded complexes with the longest perfluorocarbon chains are not. This fact is particularly interesting as it could be related to the role played by the length of the hydrocarbon alkyl chain that now it is important enough to kill the liquid crystallinity. Our objective for the next months will be to rationalize the subtle interplay between hydrocarbon and perfluorocarbon alkyl chains in the structure. The results coming from these studies will be later submitted for publication.

As concerns the use of different naked anions of organic salts as acceptors of electrons in halogen bonding-based recognition processes with halo-perfluoroalkanes, our attention turned on the use of tetra-alkyl and -aryl onium salts, like quaternary ammonium and phosphonium salts, as acceptors of halogen bonding. These organic salts, in fact, find applications as catalysts in *phase-transfer-catalysis* (PTC) processes thanks to the separation between cationic and anionic sites as a consequence of the steric hindrance induced by the alkyl and aryl substituents. The counterions of these onium salts thus become particularly nucleophilic and coordinate strongly the iodo-PFCs giving rise to binary supramolecular architectures. These tetra-alkyl onium salts were challenged with monohaloperfluorocarbons in order to obtain discrete supramolecular aggregates, which can be considered noncovalent analogues of fluorinated surfactants.

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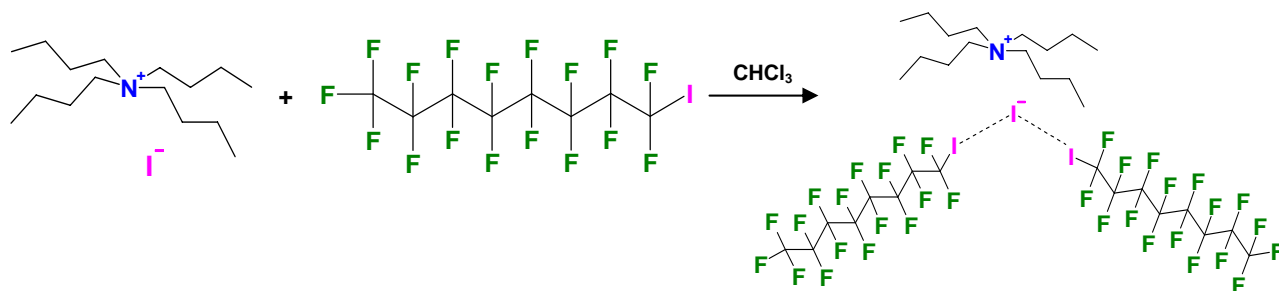
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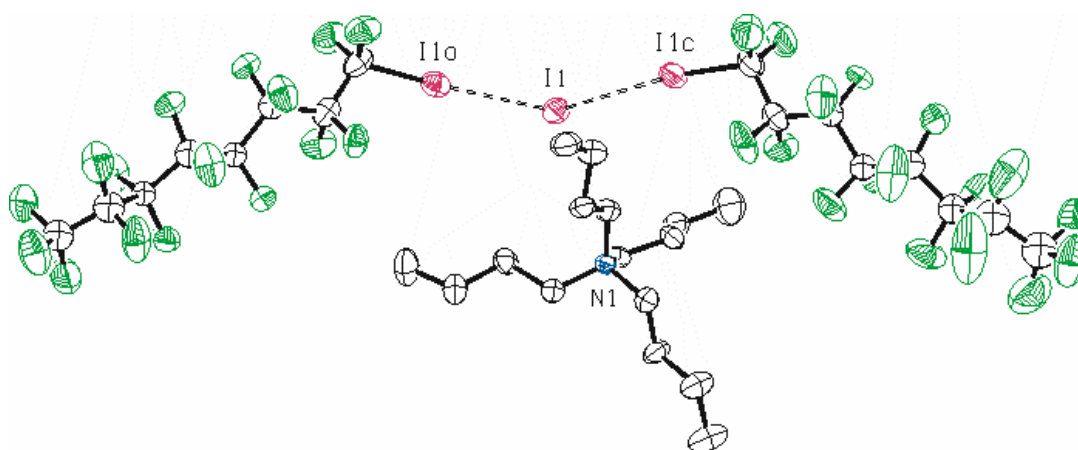
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Tetrabutyl ammonium iodide has been challenged first with 1-iodoperfluorooctane (Scheme 5).



**Scheme 5**

As demonstrated by NMR, DSC, and IR the two species give rise to a 1:2 supramolecular halogen-bonded adduct. Crystals of this binary system suitable for X-ray diffraction characterization were grown from  $\text{CHCl}_3$ . As demonstrated from the single crystal X-ray structure of the complex between tetrabutyl ammonium iodide and 1-iodoperfluorooctane (Figure 6), discrete trimeric halogen-bonded supramolecular adducts are obtained, wherein the naked  $\text{I}^-$  ions behave as bidentate halogen-bonding acceptors towards two molecules of 1-iodoperfluorooctane, which in turn behaves as halogen-bonding donor.



**Figure 6**

Finally, it has been studied the solution behavior and phase transfer properties of the complex between tetrabutyl ammonium iodide and 1-iodoperfluorooctane. While tetrabutyl ammonium iodide is not soluble in benzene at all (Figure 7, a), 1-iodoperfluorooctane is miscible with benzene at room temperature (Figure 7, c). We found that by heating at 80 °C a benzene solution (1 mL) containing 164 mg of tetrabutyl ammonium iodide in the

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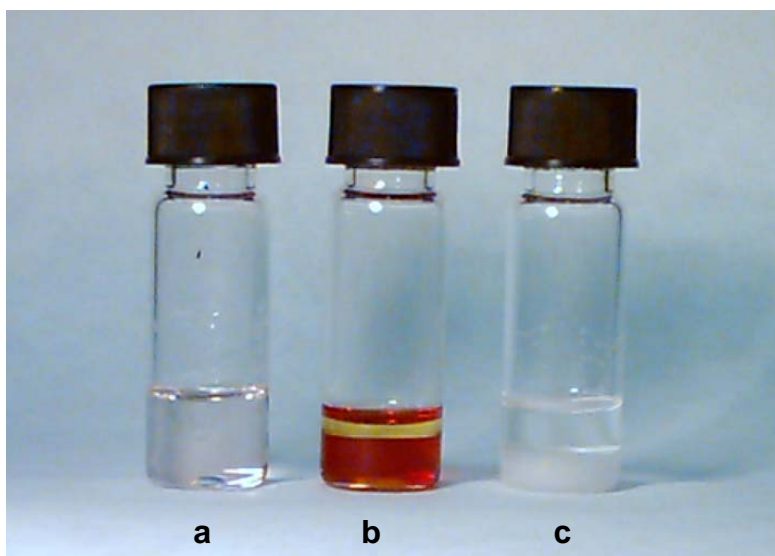
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presence of 1 eq of 1-iodoperfluorooctane (111 mg), after 5 hours we obtained the complete dissolution of the solid tetrabutyl ammonium iodide with the formation of a biphasic liquid system constituted by 0.8 mL of a heavy and dense orange solution with 0.2 mL of a clearer and less dense solution on top (Figure 7, b).



**Figure 7**

The nature, composition, and general occurrence of the above described phenomenon are in good agreement with a possible role of the tetrabutyl ammonium iodide/1-iodoperfluorooctane binary system as surfactant and will be the focus of a publication on the topic which will be submitted for publication on a specialized journal.

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